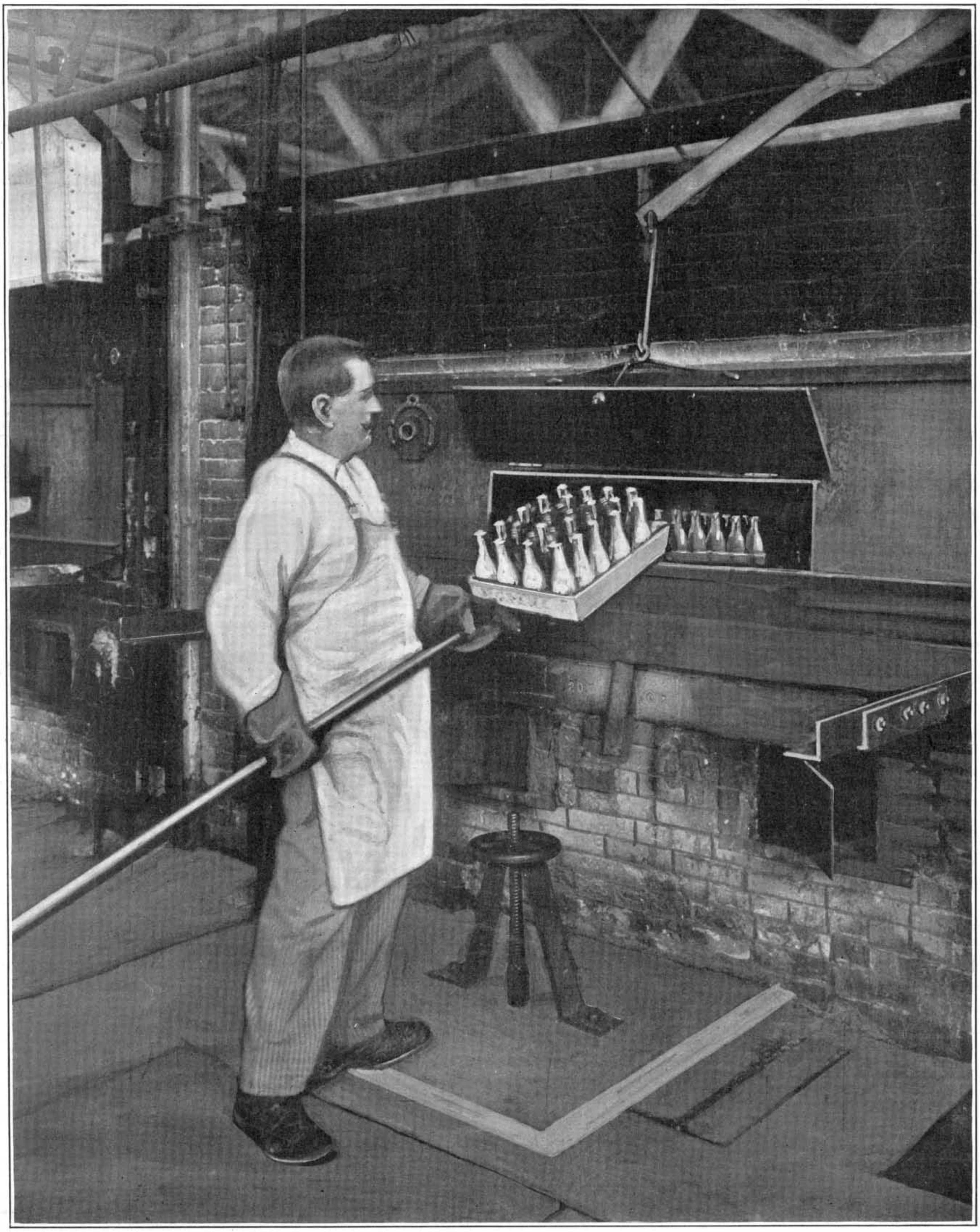
SCIENTIFIC AMERICAN SUPPLEMENT

Copyright 1916 by Munn & Co., Inc.

VOLUME LXXXII
NUMBER 2135

★NEW YORK, DECEMBER 2, 1916★

10 CENTS A COPY
$5.00 A YEAR



Press Illustrating Service, Inc.

Newly molded bottles are slowly cooled in an annealing oven to make the glass tough and less liable to break.

THE MANUFACTURE OF BOTTLES.—[See page 360.]

Rontgen Rays and Crystal Structure*

A Study of How Atoms Are Grouped in Solids

To the general public the Röntgen rays remain the X-rays—the name chosen by their discoverer—a scientific mystery, more fascinating than radium, which, after all, does not do much more than shine and decay, a thing a conservative mind does not approve of. That in decaying radium generates helium, and that the disintegration proceeds through an extraordinary series of stages, ranging in time-period from minutes to thousands of years, is hardly understood by people who are quite able to appreciate the wonderful things that medical men have achieved with the aid of Röntgen tubes. But the rays have done much more. They have helped to establish the actual existence of the atom and to reveal that the atom itself has a structure, and they promise to disclose the structure of the atoms in crystals—i. e., the way in which the atoms are grouped and arranged in solids. The student of elementary science soon grasps that solids are dreadfully complex by comparison with gases. The chemist can analyze solids as well as fluids. He splits a compound into its constituent elements, finds out the relative numbers of atoms of each constituent, counts, in conjunction with the physicist—for it is mainly physical chemistry, of course—the actual number of molecules or atoms, and assigns definite structures to the constitutions of certain substances. Those constitutions are not mere speculations; for compounds have synthetically been built up from their elements on the basis of these researches. But there science seemed to find its limit. Calcite, it has long been known, is $CaCO_3$, like limestone; in the kiln the carbonate behaves as if it were made up of CaO and CO_2; in solutions it seems to split into the ions Ca and CO_3. How are the atoms of Ca, C, O actually grouped in the crystal? If they were differently grouped, their properties would probably be different. What are the forces and the laws? The X-rays promise to answer these questions.

The X-rays first puzzled scientists by penetrating through opaque substances and by refusing to be reflected, refracted, or polarized. But there was a strong suspicion almost from the first that they were, after all, only rays of light, though of a light of extremely small wave-length, too delicate to be examined by ordinary apparatus. That assumption has been fully confirmed. The wave-length of sodium light is 5895×10^{-10} m., or Angström units (A.U.), or 5895×10^{-8} cm., and X-rays have wave-lengths of the order of 10^{-5} cm., about one ten-thousandth of the length of ordinary light waves. In a diffraction grating the spacings between the lines should be of the order of the wave-length of the incident light; that condition is fulfilled by ordinary gratings with about 20,000 lines to the inch. To rule a grating with 10,000 times as many lines would be out of the question; the distances between the lines should be of the order of inter-atomic distances. The ingenious idea occurred to Prof. M. von Laue then (in 1912) at Munich (he accepted a call to Zürich soon afterward) to make use of the ordered array of the atoms in a crystal as an X-ray grating. The experiments made by Laue in connection with W. Friedrich, P. Knipping, J. Herweg, E. Hupka and others, were surprisingly successful; crystals of zinc-blende, copper sulphide, rock salt, diamond, zinc, sulphur, etc., behaved like three-dimensional gratings. That was the origin of the new line of research. The experiments were made by letting a beam of Röntgen rays pass through a crystal on to a photographic plate; the black central spot produced on the plate was found surrounded by small dark spots of greater or smaller intensity, arranged symmetrically to the center and lying on circles or ellipses passing through the center, each spot representing a reinforcement of the waves in that direction. Crystals of copper sulphate gave such a radiograph, the powdered crystals did not. But long exposures (of many hours often) were required, and the interpretation of the radiographs in all their striking regularity, as given by Laue, was very complex; he published a memoir on the "Diffraction of Short Electromagnetic Waves by a Crystal" in the *Berichte* of the Bavarian Academy, Munich, June, 1912.

In a mathematical discussion of this memoir (*Proceedings* of the Cambridge Philosophical Society, February, 1913), Mr. W. Lawrence Bragg, of Cambridge, proposed a simpler interpretation of the phenomena, which he illustrated by the diagram, Fig. 1. Let a beam of homogeneous light A, A_1, A_2, A_3 of wave-length λ fall on a series of plane parallel surfaces p (all at the same distance apart d), each of which reflects a small proportion of the incident light and transmits the remainder; then reflection and interference will result as with thin films, except that there are a great many reflecting surfaces instead of the two of the soap film. The wave A B will partly be reflected, at its angle of incidence θ, in the direction B C, and will partly travel on into the crystal; this latter portion is not indicated in the diagram. The waves reflected at B^1, B^{11}, B^{111}, etc., will, under certain conditions, pass out in the same direction B C, and in the same phase. To find the conditions, draw B N at right angles to A^1, B^1 and produce A^1, B^1 until it cuts the plane B^{11} in D, which will be the mirror image of the point B in plane B^{11}; since then $B^1 B = B^1 D$, $A B = A^1 D$, and $N D = B^1 D$ (the distance by which the rays A B and $A^1 B^1$, and hence also the broken rays A B C and $A^1 B^1 C$, will differ) will be $2\,d \sin \theta$. If D N be equal to the wave-length λ or to a multiple of it, the waves reflected at B and B^1 and similarly at B^{11}, etc., will all be in the same phase and reinforce one another. If D N differ only slightly from λ, the difference in phase will become greater and greater as the number of planes increases, and the resultant amplitude at C will practically be zero. Thus reflection (as different from ordinary reflection) will only take place when $\lambda = 2\,d \sin \theta$. This will be a reflection of the first order, and to mark this we write $\lambda = 2\,d \sin \theta_1$. If θ_1 be changed to θ_2, there will be again reflection of the second order for $2\,\lambda = 2\,d \sin \theta_2$, and reflection of the third order for $2\,\lambda = 2\,d \sin \theta_3$, etc. At angles not satisfying this condition there will be no reflection.

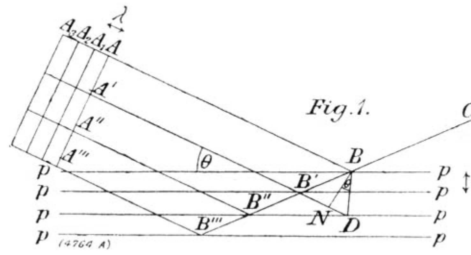


Fig. 1.

Now in a regular crystal the atoms are probably arranged in parallel planes p, thousands of planes, all at spacings d; the d may or may not be equal to the distance between two atoms next to one another in the same plane. The planes will not form continuous walls; that is not necessary for reflection, since a cluster of trees or a cloud can reflect sound waves as well nearly as a wall of rock. The atom-bearing planes are set in crystals at intervals of one or two Angström units. The characteristic X-rays used for this study are of the order of about half an Angström unit. This is a pregnant fact, to use the words of Prof. W. H. Bragg; the wave-lengths might easily have been ten or a hundred times the atom spacings, and then the investigation of crystal structure by means of X-rays would have been impossible. The method suggested by Mr. Bragg has been applied with brilliant success by Mr. Bragg himself and by his father, Prof. W. Henry Bragg, up till recently at Leeds, now at University College, London, and in this review we follow mainly the communications made by Prof. Bragg, who quite recently lectured upon the subject again before the Institute of Metals and at the Royal Institution. The Bragg method, it may broadly be said, works with reflected rays, while the Laue experiments were with transmitted rays. In their main conclusions the two methods are in entire agreement.

THE FUNDAMENTAL SPACE LATTICE

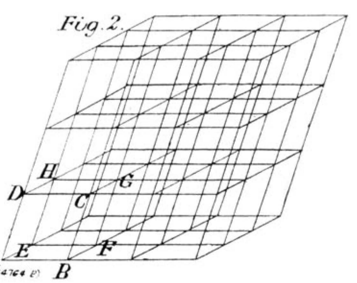


Fig. 2.

The Bragg relation, $\lambda = 2\,d \sin \theta$, may be utilized in two ways. When the λ is known, the θ are observed and the d determined; once the d values are determined, the λ can be checked. As the wave-lengths λ of X-rays have been measured by independent methods, and the θ can be measured within 1 minute of arc, the new research admits of considerable reliability. The apparatus used by Prof. Bragg is a kind of spectrometer without lenses. A pencil of homogeneous X-rays from anticathode of rhodium (or some other platinum metal) falls through two narrow slits on a crystal which is mounted on a platform; the reflected ray enters the slit of an ionization chamber (about 5 centimeters in diameter, 15 centimeters long) charged with a heavy vapor (methyl bromide is now preferred, sulphur dioxide was first used); the resulting ionization is measured by means of an electroscope and microscope. The crystal or the ionization chamber, or both together, may be turned on the platform to determine the angles at which decided reflection and ionization occur. There is always a slight diffuse reflection from the crystal surface; but the ionization maxima are easily distingushed. As natural crystal faces are often rough or distorted, the crystals are sand-papered or etched with acid, or cleavage faces are taken; elaborate preparation is not required. The rays used are the characteristic rays of the anti-cathode; rhodium emits four such rays, or two pairs, the principal ray having a λ of 0.614 Angström unit; the principal ray of palladium has a $\lambda = 0.583$, of silver 0.557 A.U., the wave-length decreasing by about 5 per cent as we pass from one atomic number to a higher number (Moseley). The ionization curve found is really the spectrum curve of these characteristic rays; with a rhodium target, therefore, the rhodium rays are repeated in the spectra of higher orders at decreasing intensity; the amplitude of the curve marks the intensity. The method thus does not give any lasting records; the reflected beam might be received on photographic paper—M. de Broglie places a cylinder of sensitized paper round the crystal—but Prof. Bragg rarely resorts to photography.

In order to elucidate the relation of the spacings to the crystal form, Prof. Bragg calls attention to wall-paper patterns. The position of any point in a pattern may be fixed with regard to two arbitrary systems of parallel lines crossing one another and cutting the pattern up into a number of rectangles or parallelograms. But unless the chosen points of intersection are the same corresponding, representative points, repeating at regular intervals, the parallelogram will not be a "unit" comprising the *ensemble* of the pattern. Similarly the atoms of crystals are referred to "space-lattices," a kind of scaffolding of three-dimensioned axes which, in the cubic system, cross all at right angles and at equal distances apart; in the other crystallographic systems the distances and angles are not all equal. When planes are passed through all the X, all the Y, and all the Z axes, the structure is cut up into cells, cubes, or parallelopipeds. Even the most complicated crystal can be referred to such a fundamental space-lattice as indicated in Fig. 2. But a cell will not necessarily be a fundamental unit, unless it comprises at least the full number of atoms making up the characteristic molecule (possibly group of molecules) of the substance. Each unit can be considered separately; but to understand the growth of crystals and the special relations, it is better to consider the space-lattice as unlimited in all directions. In the crystal models the axes are represented by wires, and the atoms by beads strung on them. Supposing the atoms to be spaced quite regularly, as in Fig. 3; each little dotted square (in the wall-paper), or each cube on that base (in the crystal), would represent a unit. In the alternating grouping of Fig. 4 each dotted square would again give a cube (1 or 2); but only one of the two (2) would represent a unit (the *c* in Fig. 4 will be explained presently); and in Fig. 5, four of the little squares would be required to make up a unit. The relations become clearer when small balls (atoms) are piled upon one another, which can be done in various ways; but the wire models are the most instructive, and when they are so held in the lantern beam (as Prof. Bragg does) that corresponding axes and atoms coincide, the arrangement of the atoms in the various planes can clearly be recognized.

When the pencil of X-rays falls on the plane A B C D (Fig. 2), the formula $\lambda = 2\,d \sin \theta$ gives the d as distance between that plane and the next parallel to it E F G H. When the pencil falls on the plane A E H D the distance of this plane from B F G C is determined. But planes may also be passed, e. g., through E B C H and corresponding points, cutting off the bevel of the edge A D; again, the nose of the crystal may be cut off, as Prof. Bragg calls it, by a plane through D and E B; and so on. The values of d determined in this way may or may not be equal; but they will always be in definite geometrical relations. The larger the angles of reflection observed the closer will be the spacing. Yet the deduction of the crystal structure from the d is not simple. In the case of a cubical lattice, for instance, the atoms may be arranged to cubes in three

---

*Engineering.